

The University of Chicago

HYPERFINE STRUCTURE IN SILVER

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE PHYS-
ICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

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Hyperfine Structure in Silver

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Twenty lines in the visible spectrum, $\lambda 7688$ in the infrared, and the two resonance lines $\lambda 3383$ and $\lambda 3281$ were studied by means of a hollow cathode source and Fabry-Perot interferometers. All lines in the visible were found to be simple in agreement with the findings of other investigators. $\lambda 7688$ was found to be a very broad line and lines

$\lambda 3383$ and $\lambda 3281$ were each found to be double with the weaker component on the longer wavelength side. Photographic plates measured gave an average of 0.055 cm^{-1} for the separation in $\lambda 3383$ and 0.056 cm^{-1} in $\lambda 3281$. It is concluded that the doubling of these lines is due to a splitting of the $5S$ level because of nuclear spin which is probably $3/2$.

SEVERAL attempts have been made recently to find hyperfine structure in the spectrum of silver. Frisch,¹ using a Schüler hollow cathode source and the fourth order of a large concave grating, found no indication of hyperfine structure in the resonance lines. Shenstone² stated that silver shows no hyperfine structure. Mohammad and Sharma³ used the Mohammad vacuum tube source with a Wehnelt oxy-cathode of platinum and an anode of silver. They used thermionic currents of from 1.5 to 2.5 amperes thinking that it was necessary to melt the silver. By means of a Lummer-Gehrke plate, they studied eighteen lines of the silver spectrum, and found all of them simple except the resonance lines. In each of these they got three components, two about equally intense and a third, on the short wavelength side, much weaker. They believed the $5S$ level of silver to be a triplet with term separations of 0.218 cm^{-1} and 0.166 cm^{-1} .

Williams and Middleton⁴ used a liquid-air cooled hollow cathode source and a reflection echelon. In order to avoid the reversal that was supposed to have given the two intense components in the results of Mohammad and Sharma, their hollow cathode was made of 95 percent cadmium and 5 percent silver. Jackson's⁵ source consisted of silver chloride in the capillary portion of a fused silica tube containing neon at a pressure of 0.5 mm Hg. He also used a reflection echelon. After calculating line widths he concluded that any separation in the resonance lines must be less than 0.07 cm^{-1} and that any

separation in the other lines must be less than 0.04 cm^{-1} . Tolansky⁶ used a water-cooled hollow cathode with fairly low currents and a silvered Fabry-Perot interferometer to study lines in the visible and infrared parts of the silver spectrum. He used interferometer spacings up to 25 mm and found all the lines studied to be simple, however, he mentioned in a note in his paper that $\lambda 7688$ was broadened and that a narrow doubling due to the term $6s^2S_{\frac{1}{2}}$ was suspected. He believed Williams' plates to show that any doubling in the resonance lines is less than 0.05 cm^{-1} .

Before the papers mentioned in the preceding paragraph were published work was started on the spectrum of silver at Ryerson Laboratory. This was continued in order to see if sufficient resolution could be obtained to detect any structure in the $5S$, $6S$ or possibly the P terms. The first source used was a simple uncooled graphite hollow cathode 8 cm long and 1.5 cm in diameter, in helium at a pressure of 3 mm Hg with current supplied by a 2000-volt d.c. generator. A small amount of metallic silver was placed inside the cathode. Exposures were made from the first to the fifth orders inclusive in the visible and near ultraviolet, on a 21-foot grating with 15,000 rulings to the inch. Currents first used were of the order of one ampere. All lines studied appeared to be simple except the resonance lines which showed reversals faintly on third order plates and quite strongly on plates of the fifth order. Another set of exposures made with the current reduced to 0.5 ampere showed no reversals and no structure in the fifth order. Eastman Process plates were used for exposures to the resonance lines.

¹ R. Frisch, *Zeits. f. Physik* **71**, 89 (1931).

² A. G. Shenstone, *Phys. Rev.* **37**, 1023 (1931).

³ W. Mohammad and C. Sharma, *Ind. J. Phys.* **6**, 75 (1931 and 1932).

⁴ W. E. Williams and A. Middleton, *Nature* **131**, 692 (1933).

⁵ D. A. Jackson, *Nature* **131**, 691 (1933).

⁶ S. Tolansky, *Proc. Phys. Soc. London* **45**, 559 (1933).

Later a larger water-cooled hollow cathode was substituted for the uncooled one. This consisted of a very thin graphite tube inserted tightly inside a thick-walled, cylindrical aluminum block that was cooled by water flowing through copper tubing around it. The anode was a nickel cylinder three inches long and one inch in diameter. The cathode was placed at the center of a three-liter flask and the anode in a side tube sealed on to the flask. The helium used was purified by allowing it to flow slowly through a charcoal trap in liquid nitrogen into a reservoir on the apparatus. Then what was used in the discharge tube was circulated through another flask where magnesium was vaporized by a heating coil. A large Fabry-Perot interferometer with silver surfaces on glass constituted the dispersive apparatus and this was mounted between the collimator and prism of a large aperture prism spectrograph.

Exposures were made with interferometer plate separations ranging from 3.5 mm to 45 mm, with currents of 1 ampere, 0.7 ampere and 0.46 ampere. Twenty lines in the visible spectrum and one in the infrared were studied. These involved terms up to $8s^2S_1$, $5p^2P_{11}$, and $7d^2D_{21}$. No structures were found.

The green lines $\lambda 5209$ ($5p^2P_1-5d^2D_{11}$), $\lambda 5465$ ($5p^2P_{11}-5d^2D_{21}$), and $\lambda 5471$ ($5p^2P_{11}-5d^2D_{11}$) were studied very carefully. The most satisfactory exposures were obtained with an interferometer separation of 25 mm and a current of 0.46 ampere, but there was no indication of structure on the plates. Microphotometer traces were made of $\lambda 5209$ and $\lambda 5465$. The peaks in these traces were very symmetrical and showed no indications of structure. Hence it was to be concluded that if there is any structure in the P terms the line component separations due to it are entirely unresolved with the apparatus used. Number VI in Fig. 1 is an example of a trace of $\lambda 5465$. Ilford Soft Gradation Panchromatic plates were used for photographing these lines.

Many exposures were made of $\lambda 7688$ ($5p^2P_1-6s^2S_1$) at the currents given above with an interferometer separation of 25 mm in an attempt to show whether or not the broadening of this line is due to a doubling. Only the broadening mentioned in the note of Tolansky's⁶

paper was observed. Eastman type N plates were used in the study of this line.

Preliminary work on the resonance lines was reported in a letter to *The Physical Review*.⁷ The same water-cooled hollow cathode source already described was used in the study of these lines but it was found that very low currents had to be used on account of self-reversals. The silver surfaced glass interferometer was replaced by one with quartz plates coated with aluminum by the evaporation process. This quartz-aluminum etalon was used with a Zeiss spectrograph having quartz lenses and a quartz prism which gave very good dispersion in the region of the resonance lines of silver. These lines were separated by approximately 1.5 millimeters on the

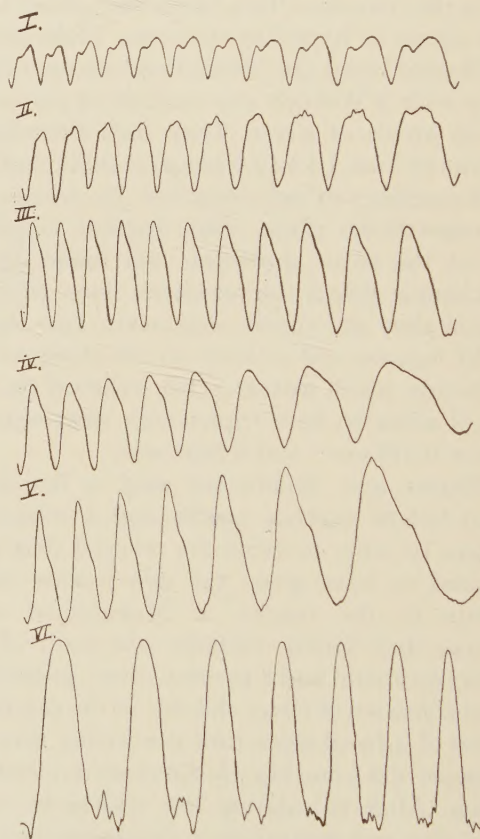


FIG. 1. Microphotometer traces of fringe systems. I, $\lambda 3383$ at 0.34 ampere, showing reversal. II, $\lambda 3383$ at 0.17 ampere, showing both the reversal and the hfs components. III and IV, $\lambda 3383$ at 0.1 ampere but each from a different series of exposures. V, $\lambda 3281$ at 0.05 ampere. VI, $\lambda 5465$ at 0.46 ampere, with $\lambda 5471$ showing faintly between the peaks of $\lambda 5465$.

⁷ H. Hill, *Phys. Rev.* **46**, 536 (1934).

plates. Etalon separators used were 32.5 mm, 26 mm, 23 mm (more accurately 22.965), 15 mm and 10 mm.

The first complete series of exposures was described in the letter referred to above. This series was made with the 23 mm spacer as the current was changed by small steps from 0.7 ampere to 0.05 ampere. At 0.7 ampere both lines are much reversed and the wing of the reversal on the longer wavelength side of each line is broader and more intense than the wing on the shorter wavelength side. The wings of the reversal of $\lambda 3281$ ($5s^2S_1 - 5p^2P_{11}$) are much farther apart than those of $\lambda 3383$ ($5s^2S_1 - 5p^2P_1$) at the same current, as might be explained by the larger J value of the P term of $\lambda 3281$, and the wing on the shorter wavelength side in one order is very near the wing on the longer wavelength side of the next lower order in the interferometer pattern.

At 0.34 ampere the reversal of $\lambda 3383$ is much reduced and a hyperfine structure component begins to show on the longer wavelength side of the line. This reversal is shown by microphotometer trace I in Fig. 1. Trace II shows that the reversal has practically disappeared at 0.17 ampere and the component on the longer wavelength side is definitely visible on the original plate. Trace III was made from an exposure at 0.1 ampere, and trace IV from another at about the same current in a later series. Traces III and IV show broadening but no sign of reversal. These and other series of exposures show quite definitely that the weaker component on the longer wavelength side of each fringe appears as the reversal disappears. It is not possible to confuse the weaker component with the weaker wing of the reversal since they appear on opposite sides of the fringes. The presence of the weaker component is probably the cause of the great lack of symmetry in the reversal. After the preliminary results were reported by letter, many other exposures were made with different currents and different helium pressures. Best results were always obtained with the 23 mm separator.

At 0.34 ampere $\lambda 3281$ has about the same appearance as $\lambda 3383$ at 0.7 ampere. At 0.17 ampere it is about the same as $\lambda 3383$ at 0.34 ampere. At 0.1 ampere it is comparable to

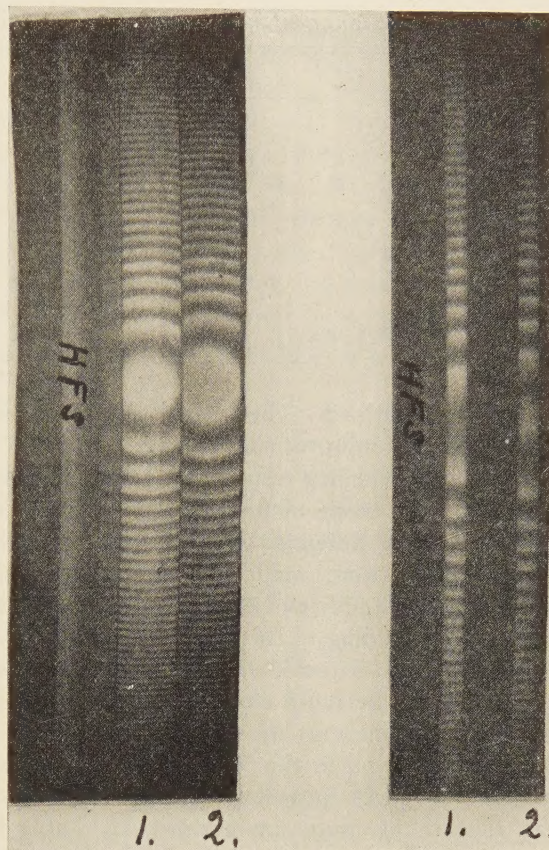


FIG. 2. 1. shows HFS of $\lambda 3281$. 2. shows HFS of $\lambda 3383$.

$\lambda 3383$ at 0.17 ampere. Microphotometer trace V of $\lambda 3281$ was made from a plate of a later series exposed at a current of 0.05 ampere. The component is shown in approximately the same manner as that shown by $\lambda 3383$ exposed at a current of 0.1 ampere or lower. The intensity at this current is naturally quite low.

The reversals did not disappear at the same currents when the helium pressure was changed. In one current-series of exposures when the pressure was reduced to about half of that used at first, one wing of the reversal of $\lambda 3281$ overlapped the other wing in the next lower order and the appearance was that of an unreversed line. Good reversals of both lines were obtained at 0.25 ampere, and that of $\lambda 3281$ persisted down to a current of approximately 0.1 ampere, however, it was not determined in this case whether or not the cooling of the cathode was the same as it had been in the first series of

TABLE I. *Line component separations.*

$\lambda 3383$	$\lambda 3281$
0.053 cm^{-1}	0.057 cm^{-1}
0.056	0.055
0.056	0.053
0.057	0.058
0.052	0.056
0.052	
0.054	0.056 cm^{-1} Average.
0.053	
0.058	
0.055 cm^{-1} Average.	

exposures described. The time of exposures ranged from 20 minutes to four hours.

For the preliminary results comparator measurements were made of four different plates of $\lambda 3383$ and two different ones of $\lambda 3281$. Later measurements were made of nine additional plates of $\lambda 3383$ and five of $\lambda 3281$, and separations calculated according to the methods outlined by Tolansky⁸ and Ritschl.⁹ These measurements which were made more carefully than the first gave values somewhat lower than the approximate values given in the letter. The maximum number of orders measured on any one plate was 35 and the minimum number 12. Table I shows these data.

Finally another series of exposures was run repeating results obtained with the different etalon spacers available. The two components were observed with the 32.5 mm and the 26 mm spacers but these spacers were not very stable and no good exposures were obtained. Good exposures were obtained with the 15 mm and the 10 mm spacers. The components of $\lambda 3383$ are still quite well resolved at an etalon separation of 15 mm, but the resolution of $\lambda 3281$ is hardly detectable. At 10 mm separation $\lambda 3383$ only indicates a double line while $\lambda 3281$ appears to be unresolved. It is evident that smaller etalon separations yield patterns not sufficiently resolved, while larger ones spread the components so far apart that the orders overlap sufficiently to mask the true effect. These facts may account for the failure of earlier investigators to obtain the true doubling of the lines.

These results differ from those of Mohammad and Sharma who used such high currents that

reversals of the lines were certainly present but they are not inconsistent with the conclusions of Tolansky and Jackson concerning the upper limit for structure.

Since no structure was found in the green lines which involve the P and D terms, and it was found in the resonance lines involving the S and P terms, the conclusion that the effect is due to a splitting of the $5S$ term seems to be justified. It could also be concluded that the broadening of $\lambda 7688$ is due to a splitting in the $6S$ term. The fact that the doubling effect shows only in the $5S$ term and not in the P terms indicates that it is due to a nuclear spin and not to an isotope shift. Silver has two isotopes, 87 and 89, about equally abundant. Tolansky⁶ considered that the mass isotope shift would be too small to be observed and need not come into consideration. If the separation is due to a nuclear spin it would be expected that the separation of the $6S$ level is smaller than that of the $5S$ level, and that separations in the P terms are very small compared to the separation in the $5S$ level in agreement with the observed results. Since the separation in the $5S$ level is small, resolution of the smaller P term separations cannot be expected with our present resolving power. The higher J value of the P term of $\lambda 3281$ leads one to expect more broadening of the two components of this line than of the two components of $\lambda 3383$ also in agreement with observed results. Resolution of the two components of $\lambda 3281$ was more difficult to secure than the resolution of the two components of $\lambda 3383$. The above conclusions have to rest on the assumption that the observed hyperfine structure is due to a superposition of nearly identical patterns belonging to the two isotopes of silver.

A few attempts were made toward measuring intensity ratios of the components of the silver resonance lines but the difficulties are at present too great to warrant a very definite conclusion. Many calibrations of the Eastman Process plates were made following approximately the method used by Granath and Van Atta¹⁰ in their work on the resonance lines of sodium. The etalon was removed from the apparatus, the collimator slit

⁸ S. Tolansky, J. Sci. Inst. 8, 223 (1931).

⁹ R. Ritschl, Zeits. f. Physik 79, 3 (1932).

¹⁰ L. P. Granath and C. M. Van Atta, Phys. Rev. 44, 935 (1933).

was made wider and a series of exposures at different times made on the same plate. Microphotometer traces of these were run on the same paper with traces of corresponding interferometer patterns, but the plate calibrations in the case of silver were only used in selecting the peaks of the traces to be analyzed. The greater lack of resolution in the microphotometer traces of the silver lines made the analysis of the peaks more difficult than the example shown by Granath and Van Atta for sodium. The resolution of the silver resonance lines obtained to date does not justify making such corrections as are mentioned by Tolansky and Heard¹¹ in their work on the fine structure multiplet of As II. The intensity calibrations and the microphotometer traces showed that possibly the fourth to eighth fringes inclusive might give approximately the intensity ratio of the two components of $\lambda 3383$.

¹¹ S. Tolansky and I. F. Heard, Proc. Roy. Soc. A146, 818 (1934).

Traces of $\lambda 3281$, taken from exposures of very low intensity due to the very low currents that had to be used, showed too much variation and hence were not measured. Traces from seven plates of $\lambda 3383$ were measured giving the following averages: 1.87, 1.54, 1.80, 1.85, 1.64, 1.76, 1.72; with a general average of 1.74. This average lies between 3, the theoretical value for the intensity ratio when I is $\frac{1}{2}$ (if it is supposed that the spectral line has only two components, in this case originating from the 2S lower level), and 1.67 the theoretical value when I is $3/2$. If the structure is due to a spin, and half integral values only are to be considered because the mass numbers of both isotopes are odd, then 1.74 suggests that the nuclear spin of silver is $3/2$.

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